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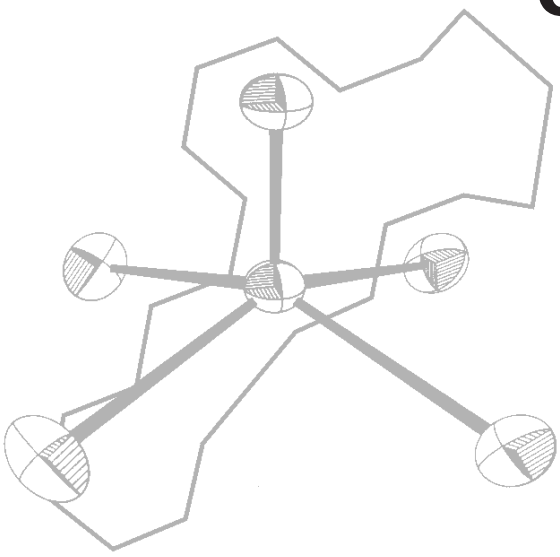

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Studies in the Cyclopropparene Series: Approaches to Cyclopropa[*b*]tetracenes

Brian Halton,[A] *David A. C. Evans*[B] *and Ronald N. Warrener*[B]

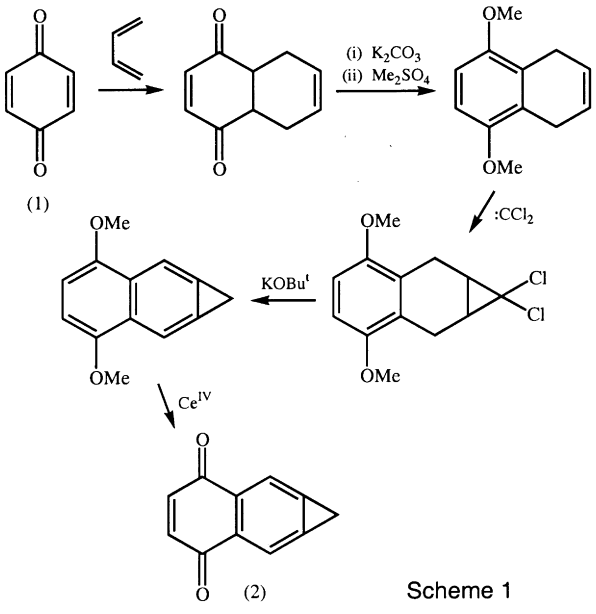
[A] School of Chemical and Physical Sciences, Victoria University of Wellington, P.O. Box 600, Wellington, New Zealand.
Author to whom correspondence may be addressed.
[B] Centre for Molecular Architecture, Central Queensland University, Rockhampton, Qld. 4702.

Cyclopropa[*b*]naphthalene-3,6-dione (2) fails to add furan across the enedione olefinic bond in a Diels–Alder cycloaddition even at 14×10^5 kPa. In contrast, isobenzofuran (4) adds efficiently at ambient temperature and pressure. The epoxytetracenedione (5) that is formed is air-sensitive and decomposes under conditions employed for dehydration. Aromatization of (5) to cyclopropatetracenedione (6) is not observed despite anthracene-1,4-dione (8) being obtained from its analogous tetrahydro precursor (7) under the same conditions.

Despite wide ranging studies of the cyclopropparene hydrocarbons,[1,2] the limit of cyclopropa-fusion into a linear aromatic acene hydrocarbon appears to be anthracene.[3] To the best of our knowledge there are no accounts describing attempts to provide cyclopropatetracenes or higher homologues. However, the recent availability of cyclopropanaphthalenedione (2) as a stable crystalline compound[4] provides a substrate eminently suitable for ring homologation by way of Diels–Alder chemistry at the enedione carbon–carbon double bond. This can allow for sequential or simultaneous extension of the ring system from naphthalene to anthracene to tetracene. We provide here the details of our approach to cyclopropa[*b*]tetracene-3,10-dione (6).

The involvement of cyclopropparenes and their derivatives in cycloadditions dates to the first isolation of parent cyclopropabenzene and involves competition between the strained C 1a–C 5a bridge bond and the lateral three-membered ring C 1–C 1a σ bond.[2] Cyclopropa quinone (2) is now easily available from benzoquinone (1) (Scheme 1),[4] and it carries a recognized dienophile in the form of the enedione carbon–carbon double bond in addition to the distorted C 1a–C 7a bridge bond; both of these sites are contenders for Diels–Alder cycloadditions.[4] Furthermore, opening of the three-membered ring by $[_\sigma2+_\pi2]$ or $[_\sigma2+_\pi4]$ addition to the strained σ bond is well documented and might also be expected to occur.[5] Competition between the three reaction centres, and the dominance of any one of them in a given reaction, will depend upon the nature of the diene, the nature of the cyclopropparene, and the conditions employed for the reaction. In this regard quinone (2) competitively adds buta-1,3-diene across the olefinic bond and the strained σ bond in a reaction that is temperature-dependent but excludes the strained bridge bond.[6]

The addition of furan to a quinone frequently is not the simplest reaction to effect because of the instability of the product, and use of high pressure is often needed.[7] This has been found true for its reaction with (2) as no evidence for product formation was obtained even when (2) and furan were subjected to a pressure of 14 kbar for 65 h at temperatures up to 45°; cyclopropa quinone and furan were returned unchanged. At the same high pressure but 65°, the quinone decomposed to an insoluble polymer that provided no spectroscopic evidence for the cycloaddition to have occurred. In contrast to the behaviour of furan, its 10 π-electron homologue isobenzofuran (4)[8] is markedly more reactive and adds to benzoquinone in good (77%) yield at ambient temperature (Experimental section).



Scheme 1

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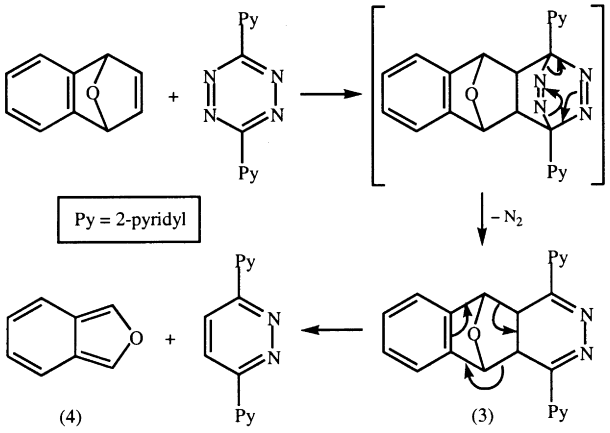
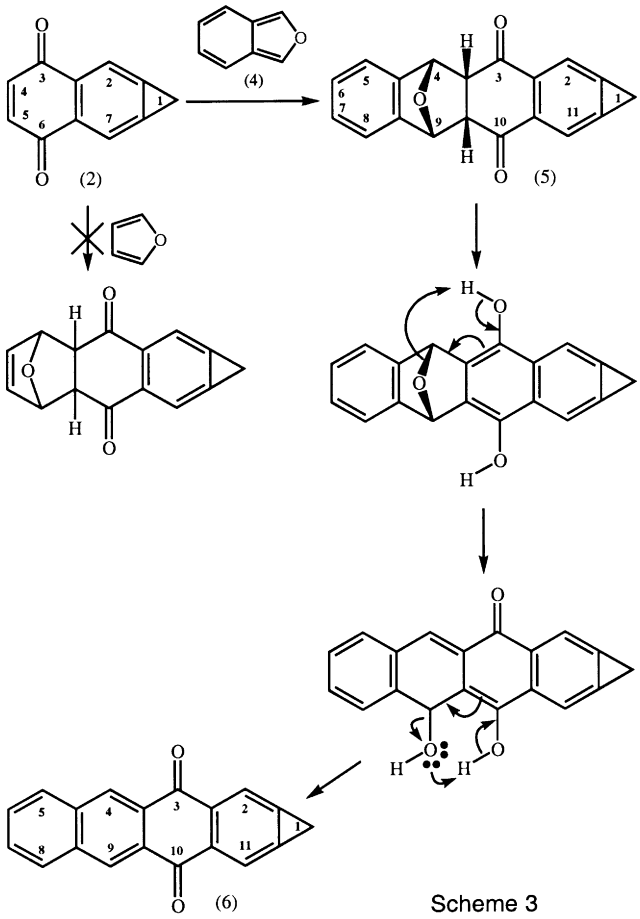
Isobenzofuran (4) is conveniently generated *in situ* and this is best achieved by way of Diels–Alder addition of 3,6-di(2-pyridyl)-1,2,4,5-tetrazine to 1,4-dihydro-1,4-epoxynaphthalene (Scheme 2).[9] The initial [4+2] cycloaddition is followed by rapid loss of molecular nitrogen with formation of the thermally sensitive diazine (3) that undergoes retro-Diels–Alder cleavage (either spontaneously from the heat liberated in the first sequence or by gentle warming), and isobenzofuran (4) is formed together with 3,6-di(2-pyridyl)-pyridazine. Generated in this way in the presence of quinone (2), diene (4) adds to the C 4–C 5 double bond to give the epoxytetracene (5) in yields of 50–70% (Scheme 3). The conversion can be made quantitative by employing an excess of diene (4) but it is more desirable to repeat the reaction sequence for a second time using *c.* 30% of the reagents (Experimental section). There is no detectable reaction between (2) and the tetrazine, and isobenzofuran (4) is not intercepted by the quinone (5) across either the C 1a–C 11a bridge bond or the C 1–C 1a σ bond.



Scheme 2

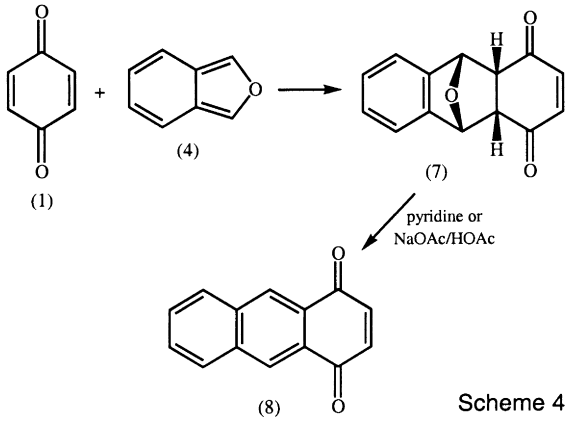
While the n.m.r. spectra recorded confirm the formation of epoxytetracene (5) all attempts to isolate the pure compound have been frustrated by its ease of decomposition. Conventional workup leads to the removal of the organic bases but the significant discoloration is accompanied by the formation of insoluble materials; subsequent attempts to purify (5) by radial chromatography resulted in the loss of the compound. Rapid filtration through a short column of silica gel, however, provided a small quantity of (5) as a colourless gum (*c.* 12%) that was free of contaminants and had an orange fluorescence on irradiation at 350 nm. Structure (5) is assigned to this compound with confidence from the observation of a molecular ion in the electron impact mass spectrum, and a protonated molecular ion in the chemical ionization mass spectrum, respectively. The ^{1}H n.m.r. spectrum shows that the cycloaddition is across the C 4–C 5 π bond of (2) to give the *endo* adduct (5) as the C 4/9 bridgehead protons (δ 5.87) are coupled to the C 3a/9a bridge protons (δ 3.83); there is no evidence for the formation of *exo* adduct. The non-equivalent methylene protons of (5) are a closely spaced AB system (*J* 7.4 Hz) at 3.18 and



Scheme 3

3.21 ppm, respectively, and H 2/11 appear as a singlet at 7.58 ppm with the remaining four aromatic protons coupled as an AA′BB′ pattern. The molecular symmetry is evident from the appearance of 10 resonances for the 19 carbon atoms, and the shielding expected[2] for C 2/11 of the cycloproparene (δ 111.6) is clearly evident. The C 4/9 and C 3a/9a bridgehead and bridge carbons resonate at 81.8 and 48.8 ppm, respectively.

Removal of the oxygen bridge and aromatization of an epoxy dione such as (5) can be achieved with comparative ease under mild reaction conditions in a procedure that has been referred to but not previously published.[10] Thus, the *endo* adduct (7) derived from 1,4-benzoquinone (1) and isobenzofuran (4) (Scheme 4) is dehydrated with pyridine at



Scheme 4

80° to give anthracene-1,4-dione (8) in 58% yield; the reaction sequence involved is as illustrated for (5) in Scheme 3. With adduct (7) the use of sodium acetate in refluxing acetic acid also brings about the dehydration efficiently. However, as the three-membered ring of a cycloproparene is sensitive to electrophiles[2] the dehydration of (5) was attempted with pyridine rather than acetate/acetic acid. Moreover, as the three-membered ring σ bond of cyclopropabenzene is cleaved[11] upon heating at 80°, the thermal stability of (5) was examined. Epoxytetracene (5) was found to be stable at 58° over 95 h in chloroform, and thus attempts to remove the C 4/C 9 oxygen bridge were made at temperatures no higher than this. After heating cycloproparene (5) for 1 h with pyridine decomposition was evident as the ^{1}H n.m.r. spectrum no longer displayed meaningful resonances; workup provided a bright yellow glass that had no proton signals compatible with the sought after tetracene (6). Alternative approaches to the desired ring system form a part of our continuing studies.

Experimental

General

Melting points were recorded on a Gallenkamp digital melting point apparatus and are uncorrected. ^{1}H n.m.r. spectra were recorded for (D)chloroform solutions on Bruker AM300 or AVANCE DPX400 MHz instruments with ^{13}C spectra obtained from the latter; tetramethylsilane was internal standard unless otherwise stated. The assignments made have been confirmed with the aid of HETCOR ^{1}H–^{13}C correlations. High-resolution mass spectra were recorded on a Micromass AutoSpec instrument. Flash column filtrations and column and radial chromatography employed silica gel as the stationary phase with dichloromethane or acetone as the eluent.

*Attempted Cycloaddition of 1*H*-Cyclopropa[*b*]naphthalene-3,6-dione (2) to Furan*

To a solution of dione (2)[4] (20 mg, 0.1176 mmol) in dichloromethane (1.5 ml) in a pressure cell was added an excess of furan (3 drops). The vessel was closed and pressurized to 14 kbar (14×10^5 kPa). After 65 h the pressure was released and 1 drop of the solution added to (D)chloroform. The ^{1}H n.m.r. spectrum showed the presence of starting materials only. After adding 1 drop extra of furan, the pressure cell was resealed, repressurized (14 kbar) and heated at 45° for 65 h; the outcome was unchanged.

Resealing the vessel and heating at 67° and 14 kbar for 90 h led to a solution that contained furan together with an insoluble deposit. The ^{1}H n.m.r. spectrum of the deposit [suspension in (D)chloroform] showed no evidence for the desired adduct and its insolubility in all common solvents (chloroform, dichloromethane, methanol, ethyl acetate, and acetone) implies polymer formation.

*Cycloaddition of 1*H*-Cyclopropa[*b*]naphthalene-3,6-dione (2) to Isobenzofuran (4)—(3aα,4α,9α,9aα)-3a,4,9,9a-Tetrahydro-4,9-epoxy-1*H*-cyclopropatetracene-3,10-dione (5)*

To a mixture of quinone (2) (60 mg, 0.353 mmol),[4] 1,4-dihydro-1,4-epoxynaphthalene[9] (51 mg, 0.354 mmol) and 3,6-(di-2-pyridyl)-1,2,4,5-tetrazine[9] (84 mg, 0.355 mmol) in a round bottomed flask (5 ml) was added chloroform (1.5 ml). Nitrogen evolution from the purple mixture began almost immediately, the solution warmed to *c.* 40° and the colour was discharged to brown over *c.* 1 h. After 90 min, the solution was poured into dichloromethane (10 ml), washed with HCl (1 M, 10 ml), H_2O (2×5 ml), and the organic phase dried ($MgSO_4$) and concentrated in vacuum to a brown solid. The ^{1}H n.m.r. spectrum of the crude product showed adduct (5) and unchanged quinone (2) in a ratio of *c.* 7 : 3.

Resubjection of the mixture to isobenzofuran (4) [from dihydroepoxynaphthalene (17 mg, 0.118 mmol) and the tetrazine (28 mg, 0.1186 mmol) in chloroform (1 ml)] and workup as before provided a brown solid free from unchanged (2) but containing side-products from (4) and decomposition materials (n.m.r.). While attempts to purify the product by radial chromatography (plate thickness 2 mm; dichloromethane elution) provided none of the desired product, filtration through a short column (1.5 cm by 10 cm) of SiO_2 (dichloromethane elution) gave four fractions of which the third was the *title adduct (5)* as an essentially pure colourless gum (12 mg, 12%) that darkened and became brown on standing (Found: M^+ 288.0787. $C_{19}H_{12}O_3$ requires 288.0786. Found (c.i.): $[M+H]^+$ 289.0862. $[C_{19}H_{13}O_3]^+$ requires 289.0865). ^{1}H n.m.r. δ 3.18, d, *J* 7.4 Hz, 1H, C**H**$_A$H$_B$; 3.21, d, *J* 7.4 Hz, 1H, CH$_A$**H**$_B$; 3.83, app. dd, *J* 2.0, 3.6 Hz, 2H, H 3a/9a; 5.87, app. dd, *J* 2.0, 3.6 Hz, 2H, H 4/9; 6.82–6.89, AA′, 2H, H 6/7 or H 5/8; 7.03–7.09, BB′, 2H, H 5/8 or H 6/7; 7.58, s, 2H, H 2/11. ^{13}C n.m.r. δ 18.2, C 1; 48.8, C 3a/9a; 81.8, C 4/9; 111.6, C 2/11; 120.0, C 5/8 or C 6/7; 126.5, C 6/7 or C 5/8; 131.7, C 1a/11a; 137.2 and 140.9, C 2a/10 and C 4a/8a; 193.4, CO. All attempts to crystallize the gum resulted in significant darkening of the sample without formation of solid; aerial oxidation is presumed to have occurred. In the absence of air and in (D)chloroform solution adduct (5) was found to be stable for days and was held without change at 58° for a period of 95 h.

Attempted Aromatization of Adduct (5) by Dehydration

A sample of adduct (5) (*c.* 4 mg) dissolved in (D_5)pyridine was unchanged at ambient temperature over 1 h. ^{1}H n.m.r. δ 2.83, d, *J* 7.3 Hz, 1H, C**H**$_A$H$_B$; 2.92, d, *J* 7.3 Hz, 1H, CH$_A$**H**$_B$; 3.97, br s, H 3a/9a; 6.00, br s, H 4/9; 6.70–6.74, AA′, 2H; 7.47, s, H 2/11 (the BB′ component was overlapped by a solvent peak). Upon warming to 58° for 1 h the ^{1}H n.m.r. spectrum changed and showed *no* signals compatible with (5), its dehydration product (6) or a dimeric species from either.

(4aα,9α,9aα,10α)-4a,9,9a,10-Tetrahydro-9,10-epoxyanthracene-1,4-dione (7)

To a mixture of 1,4-dihydro-1,4-epoxynaphthalene[9] (225 mg, 1.56 mmol), 3,6-di(2′-pyridyl)-1,2,4,5-tetrazine[9] (370 mg, 1.57 mmol) and 1,4-benzoquinone (1) (169 mg, 1.57 mmol) in a round bottomed flask was added chloroform (5 ml). After the evolution of nitrogen ceased the mixture was diluted with chloroform (20 ml), washed with HCl (0.5 M, 2×20 ml) and the organic phase separated, dried, and evaporated to dryness. The residue was chromatographed on silica first with chloroform as eluent to remove unchanged benzoquinone and then acetone to elute *the title adduct (7)* (271 mg, 77%) which crystallized (methanol) as colourless needles, m.p. 148–150° (Found: C, 74.3; H, 4.7%; M^+, 266.0626. $C_{14}H_{10}O_3$ requires C, 74.3; H, 4.5%; M^+, 226.0629). I.r. ν_{max} 1674s, 1304m, 1291s, 1156w, 1134w, 1052m, 988m, 761m, 744w, 790m, 875m, 842m, 763s, 722w cm^{-1}. U.v. λ_{max} (EtOH) 228 (ε 10313), 262sh (992), 269 nm (728). ^{1}H n.m.r. δ 3.55–3.62, m, H 4a/9a; 5.72–5.79, m. H 9/10; 6.00, s, H 2/3; 7.15, s, 4H, aromatic. Mass spectrum *m/z* 266 (M^+, 3%), 119 (10), 118 (100), 115 (8), 90 (6), 89 (7).

Anthracene-1,4-dione (8)

Method A. The tetrahydro epoxy quinone (7) (25 mg, 0.84 mmol) was heated in pyridine (3 ml) at 80° overnight. The solution was poured into hydrochloric acid (0.5 M, 50 ml) and extracted with chloroform (2×25 ml). The combined organic extracts were dried, concentrated in vacuum and the residue was chromatographed over silica (chloroform elution) to afford yellow needles of anthracene-1,4-dione (8) (13 mg, 58%) which was purified by vacuum sublimation (150°/0.2 mmHg), m.p. *c.* 160° (sublim.) (lit.[12] m.p. 225°). ^{1}H n.m.r. δ 7.06, s, 2H, H 2, H 3; 7.78–7.57, m 2H, aromatic; 7.97–8.12, m, 2H, aromatic; 8.61, s, 2H, H 9, H 10. Mass spectrum *m/z* 210 (5%), 209 (17), 208 (M^+, 93), 180 (21), 152 (51), 126 (38), 118 (100), 97 (25), 83 (21), 71 (27), 63 (21), 56 (40), 43 (50), 41 (30), all other peaks less than 20%.

Method B. Tetrahydro epoxy dione (7) (13 mg, 0.56 mmol) and anhydrous sodium acetate (34 mg, 0.41 mmol) in glacial acetic acid (5 ml) were refluxed under a nitrogen atmosphere for 1 h. After cooling the solution was poured into water (50 ml) and the aqueous mixture extracted with chloroform (50 ml). The organic extract was separated, dried, and the solvent removed to afford anthracene-1,4-dione (8) that was purified by vacuum sublimation, m.p. *c.* 160° (sublim.), identical to the sample from above.

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Ms C. S. Jones (Victoria University) kindly provided the sample of quinone (2) that enabled these studies to be performed at the Centre for Molecular Architecture (CMA) of Central Queensland University. A visiting professorship (to B.H.) with financial assistance from the CMA and Victoria University is gratefully acknowledged. B.H. thanks the members of the CMA for their generous and genial hospitality.

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